Effect of Crystallizable Solvent on Phase Separation and Charge Transport in Polymer-fullerene Films

Kaewprajak A.; Lohawet K.; Wutikhun T.; Meemuk B.; Kumnorkaew P.; Sagawa T.

IOP Conf. Series: Materials Science and Engineering **229** (2017) 012015 doi:10.1088/1757-899X/229/1/012015

Effect of Crystallizable Solvent on Phase Separation and Charge Transport in Polymer-fullerene Films

A Kaewprajak[1,2], K Lohawet[1], T Wutikhun[1], B Meemuk[1], P Kumnorkaew[1] and T Sagawa[2,*]

[1] National Nanotechnology Center, National Science and Technology Development Agency, 111 Thailand Science Park, Phahonyothin Rd., Khlongnueng, Khlongluang, Pathumthani 12120, Thailand.
[2] Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan.

*sagawa@energy.kyoto-u.ac.jp

Abstract. The effect of 1,3,5-trichlorobenzene (TCB) as crystallizable solvent on poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) bulk heterojunction (BHJ) was investigated. We found that phase separation of PCDTBT and $PC_{71}BM$ and formation of the condensed network of polymers were appropriately regulated by addition of TCB in the BHJ films, which were confirmed by optical microscopic, AFM, and TEM observations in addition to current-voltage analyses. Through the formation of a good continuous pathway for carrier transport by the addition of TCB, 2.5 times enhancement of the hole mobility in the BHJ film was attained from 5.82 x 10^{-5} cm^2 V^{-1} s^{-1} without TCB to 1.48 x 10^{-4} cm^2 V^{-1} s^{-1} with 20 mg ml^{-1} of TCB.

1. Introduction

Organic photovoltaics (OPVs) have been attractive because they can be prepared onto flexible substrates by using simple printing techniques. [1-3] To improve the photovoltaic performance of OPVs, morphology and charge transport in bulk heterojunction (BHJ) solar cells are important. Many methods were used to optimize the morphology of polymers and fullerenes in BHJ such as thermal annealing [4, 5], solvent annealing [6, 7] and addition of solvent additives [8, 9]. One effective method to control the morphology of polymer-fullerene is adding high boiling point additive in polymer blend such as 1,8-diiodooctane (DIO) [10], 1,8-dibromooctane [11] and chloronaphthalene [12]. The solvent additive can selectively dissolve $PC_{71}BM$, which aggregates to smaller domains and promote a better donor-acceptor network into smaller domains.

In this work, we investigated the effect of 1,3,5-trichlorobenzene (TCB) as the crystallizable solvent on phase separation and formation of the highly oriented network of polymers in terms of the improvement of charge transport in poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) BHJ films. The concentration of TCB in PCDTBT:$PC_{71}BM$ were ranged from 0 to 50 mg ml^{-1} in dichlorobenzene (DCB). We found that the appropriate amount of TCB in the PCDTBT:$PC_{71}BM$

effectively improved the morphology and formation of the condensed network of polymers, which resulted in the enhancement of the hole mobility in the BHJ films.

2. Experimental

The hole-only devices were prepared with a device structure of indium-tin-oxide (ITO) coated glass/PEDOT:PSS/polymer-fullerene/Au. The polymer and fullerene are poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) (1-Material) and [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) (American Dye Source, Inc.), respectively. The glass-ITO substrates (Geomatec, 10 Ω sq^{-1}) patterned were ultrasonically cleaned with deionized water, acetone, tetramethylammonium hydroxide (Semico clean 56), deionized water and isopropyl alcohol for every 15 min. The glass-ITO substrates were dried with heat gun and treated with UV–ozone treatment for 15 min. PEDOT:PSS (Clevios™ P VP AI 4083) after passing through a 0.45 µm filter was coated by convective deposition onto the cleaned glass-ITO substrate at 3000 µm s^{-1} solution volume at 20 µL with two time coating. The sample was annealed on hot plate at 120 °C for 20 min under atmospheric conditions. The solvent mixtures were prepared by dichlorobenzene (DCB) (Sigma-Aldrich) and 1,3,5-trichlorobenzene (TCB) (Tokyo chemical industry co. ltd.) at a concentration of 0, 10, 20, 30, 40, and 50 mg ml^{-1} stirred at 45 °C for 3 h. The mixed solvents with different concentration of TCB were added with polymer blend at same volume. The solution of polymer-fullerene from a 1:4 (w/w) of PCDTBT and $PC_{71}BM$ were dissolved with the prepared solvents of TCB and DCB at a concentration of 40 mg ml^{-1}. The solution was stirred at 45 °C for overnight until PCDTBT and $PC_{71}BM$ were dissolved completely. The polymer blend was coated on top of the PEDOT:PSS layer by convective deposition at coating speed 1250 µm s^{-1} with volume at 10 µL one time coating. The bulk-heterojunction films were kept under vacuum for 1 h. Each sample was transferred to the vacuum chamber of the thermal evaporator. The vacuum chamber was pumped down to a base pressure of 2.4 x 10^{-3} Pa. The Au electrodes with a thickness of 100 nm were deposited onto the polymer layer via thermal evaporation.

3. Results and Discussion

Figure 1 shows the preparation process of PCDTBT:$PC_{71}BM$ film by convective deposition technique. Coating process starts from injection of a microliter droplet of PCDTBT:$PC_{71}BM$:DCB:TCB mixture between the deposition blade and the glass substrate. When the substrate was moved from meniscus of polymer blend solution with constant velocity at a deposition angle (α) of 45°, a thin film of polymer blend was coated horizontal deposition on the glass substrate. TCB in the thin film of PCDTBT:$PC_{71}BM$:TCB was removed by evaporation in a vacuum oven at room temperature.

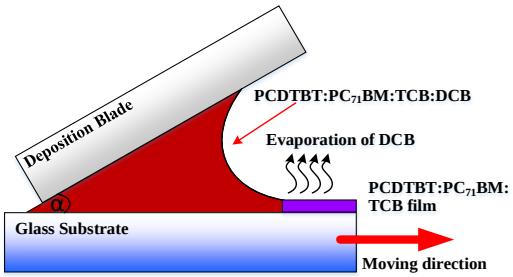

Figure 1. Schematic illustration of coating process of PCDTBT:$PC_{71}BM$:DCB:TCB solution on the glass substrate by convective deposition.

The PCDTBT:$PC_{71}BM$ films with different concentrations of TCB were observed by an optical microscope with polarized light and high dynamic range (HDR) mode as displayed in Figure 2. In Figure 2a, phase-separated fullerene-rich clusters as shown in the dark areas and polymer-rich part in the bright areas were observed. [13,14] When the amount of TCB in polymer blend film was increased

to10 and 20 mg ml^{-1}, the domains of PCDTBT-rich and $PC_{71}BM$-rich (bright and dark areas respectively) were observed as an uniformed phase separation and smaller size than those of the film without TCB as indicated in Figure 2b and 2c, respectively. When TCB concentration increased more than 20 mg ml^{-1}, the domain size of the PCDTBT-rich part and the $PC_{71}BM$-rich one gradually increased as displayed in Figure 2d to Figure 2f. The phase separated states of donor and acceptor were improved in terms of homogeneously and uniformity by the addition of TCB as a crystallizable solvent. In addition, when TCB concentration was increased more than 20 mg ml^{-1}, the domain size of donor and acceptor became larger because of aggregation of TCB at higher nucleation density.

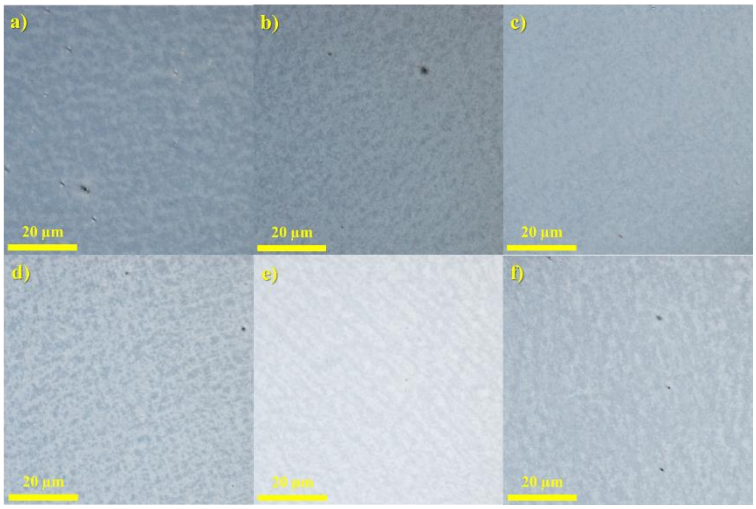

Figure 2. Optical microscopic images of PCDTBT:$PC_{71}BM$ films prepared by convective deposition with different concentrations of TCB of (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 mg ml^{-1}, respectively. Films were observed under the conditions of polarized light with high dynamic range (HDR) function. Scale bar: 20 µm.

AFM topographic images **(**5 µm x 5 µm**)** of PCDTBT:$PC_{71}BM$ films with different concentration of TCB are indicated in Figure 3. Figure 3a shows the topographic image of the film without TCB with large grain size of PCDTBT:$PC_{71}BM$. The root mean square (RMS) roughness of polymer film without TCB was 0.51 nm. When the TCB was added from 10 to 50 mg ml^{-1}, the RMS roughness were slightly increased between 0.57 and 0.65 nm. As a result of the process for elimination of TCB in the polymer blend films under the vacuum conditions, vacancy and crevice on the surface of the films might be formed.

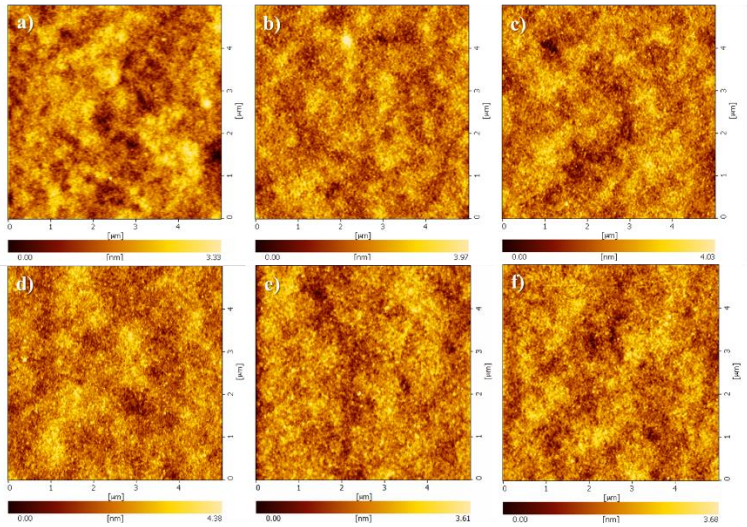

Figure 3. AFM images as tapping-mode of topography and phase mode of PCDTBT:$PC_{71}BM$ films prepared by convective deposition with different concentrations of TCB of (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 mg ml^{-1}, respectively.

Figure 4 displays the bright-field TEM images and electron diffraction (ED) patterns (insets) of PCDTBT:$PC_{71}BM$ films with different concentration of TCB. Small amount of fibrillar PCDTBT in the polymer blend films with TCB[15] was observed in Figure 4b-4f. As a result, the films with TCB had highly condensed PCDTBT network and better connected pathways for charge transport. The ED pattern of the film without TCB in Figure 4a presents a blur electron diffraction ring of its amorphous nature of PCDTBT. [16] Contrarily, crystallization of PCDTBT:$PC_{71}BM$ film with TCB was confirmed by the outer electron diffraction ring, which was indicated by white arrows right hand side of diffraction rings in Figure 4c-4f. [16]

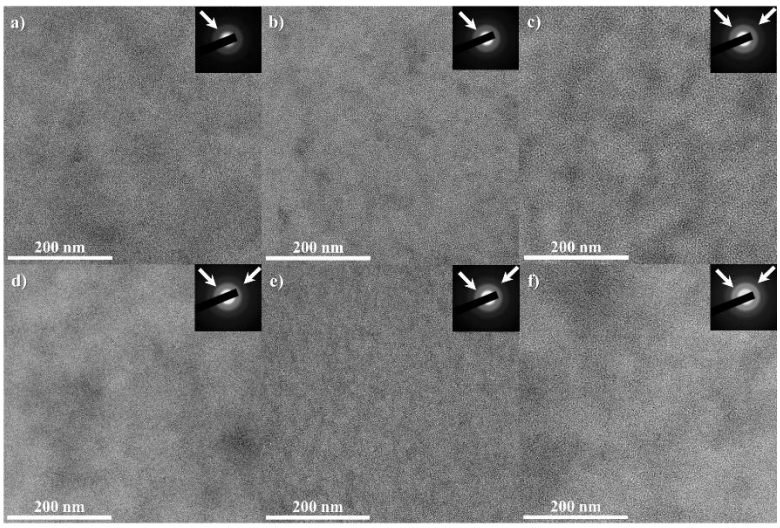

Figure 4. Bright-field TEM images of PCDTBT:$PC_{71}BM$ films prepared by convective deposition with different concentrations of TCB of (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 mg ml^{-1}. The insets are the electron diffraction patterns indicating the relative orientations to those of the bright field image.

To study the charge transport properties in the PCDTBT:$PC_{71}BM$ films, which were prepared with different TCB concentration, the hole-only devices in a configuration of glass-ITO/PEDOT:PSS/PCDTBT:$PC_{71}BM$/Au were prepared and characterized. The dark *J-V*

characteristics of the hole-only devices are displayed in Figure 5. The hole mobilities were estimated from the dark current voltage curves in Figure 5 by applying the space-charge limited current (SCLC) theory as shown in Equation (1). [17, 18]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{L^3} \quad (1)$$

Where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ_h is the hole mobility, V is the applied voltage, and L is the thickness of the polymer film. The field independent mobility in the PCDTBT:$PC_{71}BM$ film without TCB was calculated as a reference with the positive charge mobility of 5.8 x 10^{-5} cm^2 V^{-1} s^{-1}. With the concentration of TCB at 10, 20, 30, 40 and 50 mg ml^{-1}, the positive charge mobilities of the devices are 8.9 × 10^{-5}, 1.5 × 10^{-4}, 1.4 × 10^{-4}, 1.2 × 10^{-4} and 8.1 × 10^{-5} cm^2 V^{-1} s^{-1}, respectively. The maximum positive charge mobility of 1.5 × 10^{-4} cm^2 V^{-1} s^{-1} was observed when TCB concentration was 20 mg ml^{-1}. The increment of the hole mobility presumably dues to the improved crystallinity of PCDTBT, which was confirmed by the ED patterns as shown in Figure 5 and uniform phase separated states of PCDTBT and $PC_{71}BM$ in Figures 3 and 4 resulted in the formation of continuous charge pathways. [6]

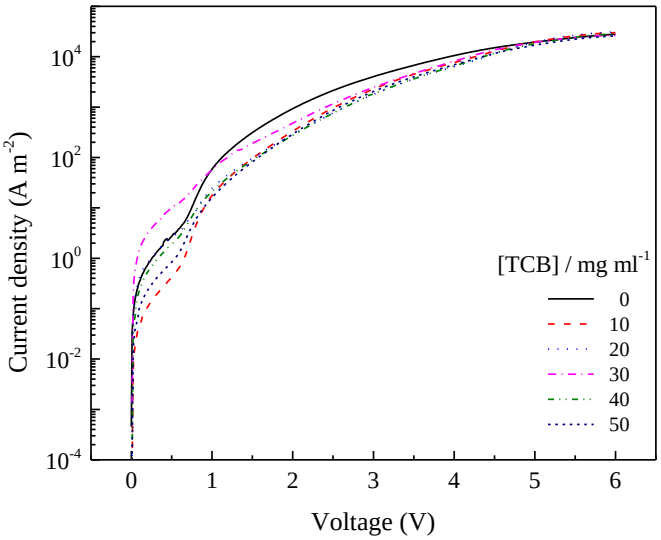

Figure 5. Dark current density (J)-voltage (V) curves of hole-only devices, consisted of glass-ITO/PEDOT:PSS/PCDTBT:$PC_{71}BM$/Au, at room temperature. The PCDTBT:$PC_{71}BM$ layers ware prepared with different concentrations of TCB from 0 to 50 mg ml^{-1}.

4. Conclusion

In conclusion, we have demonstrated the effect of TCB crystallizable solvent on the improvement of the morphology and charge transport in PCDTBT:$PC_{71}BM$ films. The films with TCB can improve of phase separated states and the domain sizes of PCDTBT and $PC_{71}BM$ bulk heterojunction. The improvement of the hole mobilities by using TCB is presumably derived from the improvement of phase separation of PCDTBT and $PC_{71}BM$, which made a formation of good continuous pathway for carrier transport. The highest hole mobility of 1.5 x 10^{-4} cm^2 V^{-1} s^{-1} in this series of the TCB addition was obtained when TCB was 20 mg ml^{-1}. That is 2.54 times improvement of hole mobility as compared to the device without TCB (5.8 x 10^{-5} cm^2 V^{-1} s^{-1}). Therefore, addition of TCB as crystallizable solvent can be effective method for improvement of phase separation of polymer-fullerene and formation of the condensed network of polymers in the BHJ films for organic electronic applications.

References

[1] Wan Q, Guo X, Wang Z, Li W, Guo B, Ma W, Zhang M, and Li Y 2016 *Adv. Funct. Mater.* **26** 6635-6640.
[2] Krebs FC 2009 *Solar Energy Mater. Solar Cells.* **93** 465-475.
[3] Gu KL, Zhou Y, Gu X, Yan H, Diao Y, Kurosawa T, Ganapathysubramanian B, Toney MF and Bao Z 2017 *Org. Electronics.* **40** 79-87.
[4] Verploegen E, Mondal R, Bettinger CJ, Sok S, Toney MF and Bao Z 2010 *Adv. Funct. Mater.* **20** 3519-3529.
[5] Kadem B, Hassan A and Cranton WJ 2016 *Mater. Sci.: Mater. Electron.* **27** 7038-7048.
[6] Liu J, Liang Q, Wang H, Li M, Han Y, Xie Z and Wang L 2014 *J. Phys. Chem. C.* **118** 4585-4595.
[7] He Z, Liu F, Wang C, Chen J, He L, Nordlund D, Wu H, Russell TP and Cao Y 2015 *Mater. Horizons.* **2** 592-597.
[8] Etzold F, Howard IA, Forler N, Cho DM, Meister M, Mangold H, Shu J, Hansen MR, Mullen K, and Laquai F 2012 *J. Am. Chem. Soc.* **134** 10569-10583.
[9] Liao H-C, Ho C-C, Chang C-Y, Jao M-H, Darling SB and Su W-F 2013 *Mater. Today.* **16** 326-336.
[10] Liang Y, Xu Z, Xia J, Tsai S-T, Wu Y, Li G, Ray C and Yu L 2010 *Adv. Mater.* **22** E135-E138.
[11] Huang D, Li Y, Xu Z, Zhao S, Zhao L and Zhao J 2015 *Phys. Chem. Chem. Phys.* **17** 8053-8060.
[12] Yi C, Hu X, Liu HC, Hu R, Hsu C-H, Zheng J and Gong X 2014 *J. Mater. Chem. C.* **3** 26-32.
[13] Piersimoni F, Degutis G, Bertho S, Vandewal K, Spoltore D, Vangerven T, Drijkoningen J, Van Bael M K, Hardy A, D'Haen J, Maes W, Vanderzande D, Nesladek M and Manca J 2013 *J. Polym. Sci. Part B: Polym. Phys.* **51** 1209-1214.
[14] Liu H-W, Chang D-Y, Chiu W-Y, Rwei S-P and Wang L. 2012 *J. Mater. Chem.* **22** 15586-15591.
[15] Park SH, Roy A, Beaupré S, Cho S, Coates N, Moon JS, Moses D, Leclerc M, Lee K and Heeger AJ 2009 *Nat. Photon.* **3** 297-302.
[16] Kim T, Jae Yang S, Kyun Kim S, Soo Choi H and Rae Park C 2014 *Nanoscale.* **6** 2847-2854.
[17] Goh C, Kline RJ, McGehee MD, Kadnikova EN and Fréchet JMJ 2005 *Appl. Phys. Lett.* **86** 122110.
[18] Wang ZB, Helander MG, Greiner MT, Qiu J and Lu ZH 2010 *J. Appl. Phys.* **107** 034506.